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(71) Applicants
United Kingdom Atomic Energy Authority, (United Kingdom), 11 Charles II Street, London SW1Y 4QP.
(72) Inventors
Dr. David Edward Williams
(74) Agent and/or Address for Service
Clive Stephen Bennett, Patents Branch, United Kingdom Atomic Energy Authority, 11 Charles II Street, London SW1Y 4QP.

(54) Solid electrolyte gas sensors

(57) A gas sensor suitable for use in a gas or gaseous mixture comprises a solid electrolyte 1, in which the mobile ion is other than oxygen, and two or more electrodes 2, 3 in communication with the said solid electrolyte and arranged so as to be capable of being contacted with a common gas or gaseous mixture.

Examples of suitable solid electrolytes are sodium-beta-alumina, hydrogen-beta-alumina and rubidium-beta-alumina.

The electrodes may be of different sizes and different materials and may be arranged to produce different potentials with the same gas.

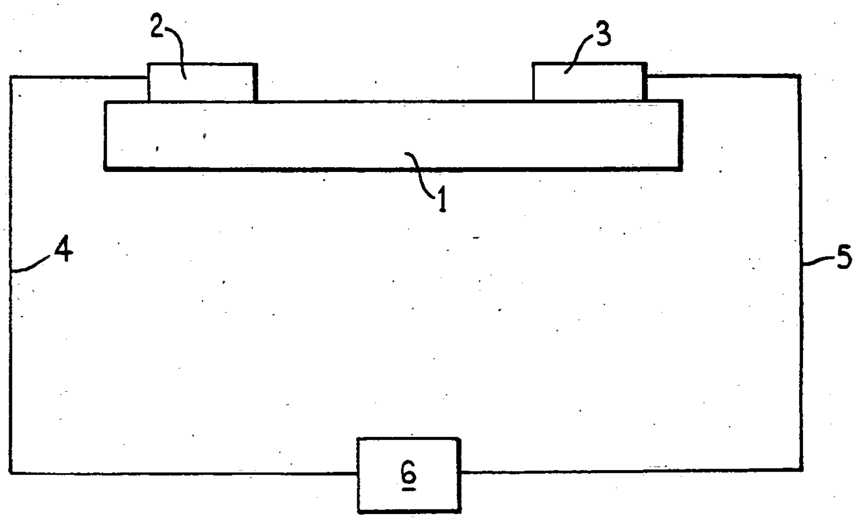

FIG. 1

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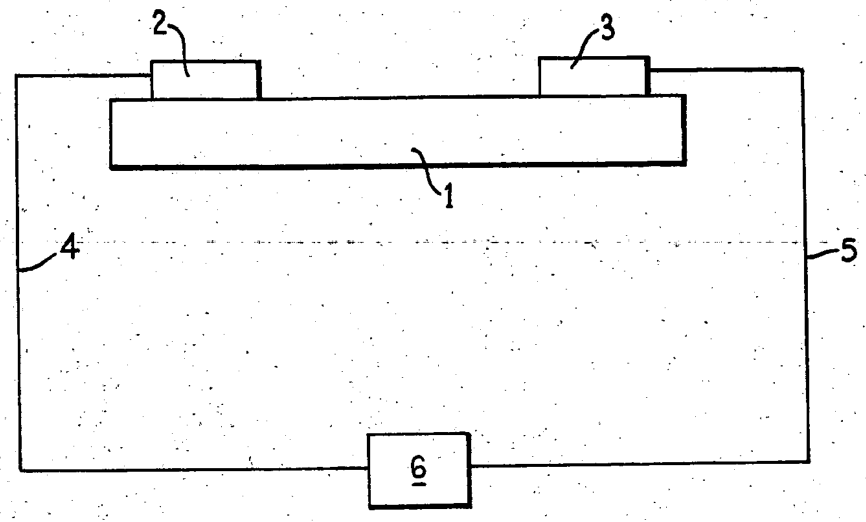
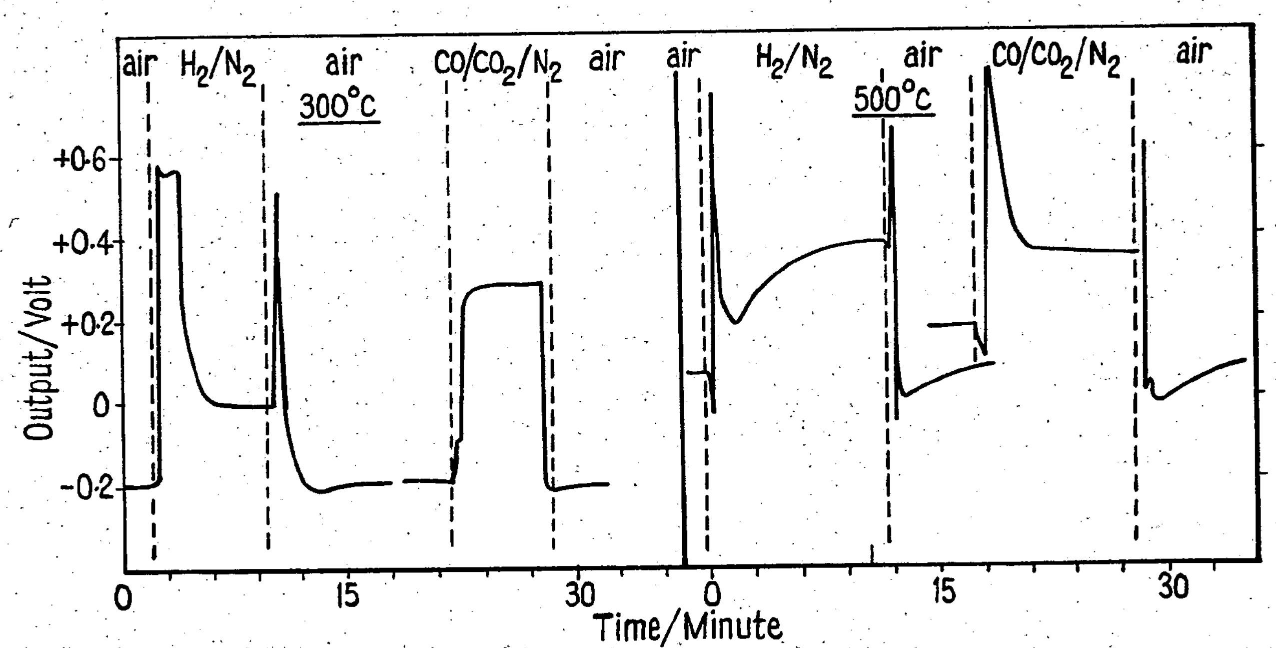

2
3
1
4
5
6

FIG.1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H_2/N_2
air
300°c
$CO/CO_2/N_2$
air
air
H_2/N_2
air
500°c
$CO/CO_2/N_2$
air
+0·6
+0·4
+0·2
0
-0·2
Output/Volt
0
15
30
0
15
30
Time/Minute

FIG.2

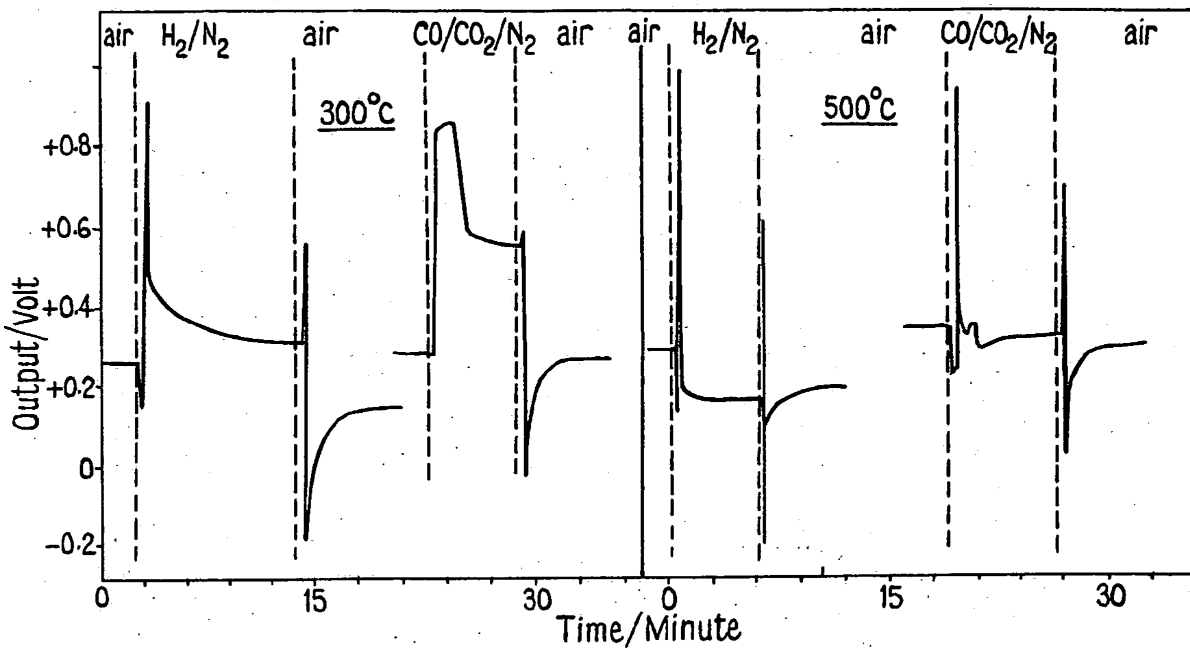
air
H_2/N_2
air
$CO/CO_2/N_2$
air
300°C
air
H_2/N_2
air
$CO/CO_2/N_2$
air
500°C
Output/Volt
+0·8
+0·6
+0·4
+0·2
0
-0·2
0
15
30
0
15
30
Time/Minute

FIG.3

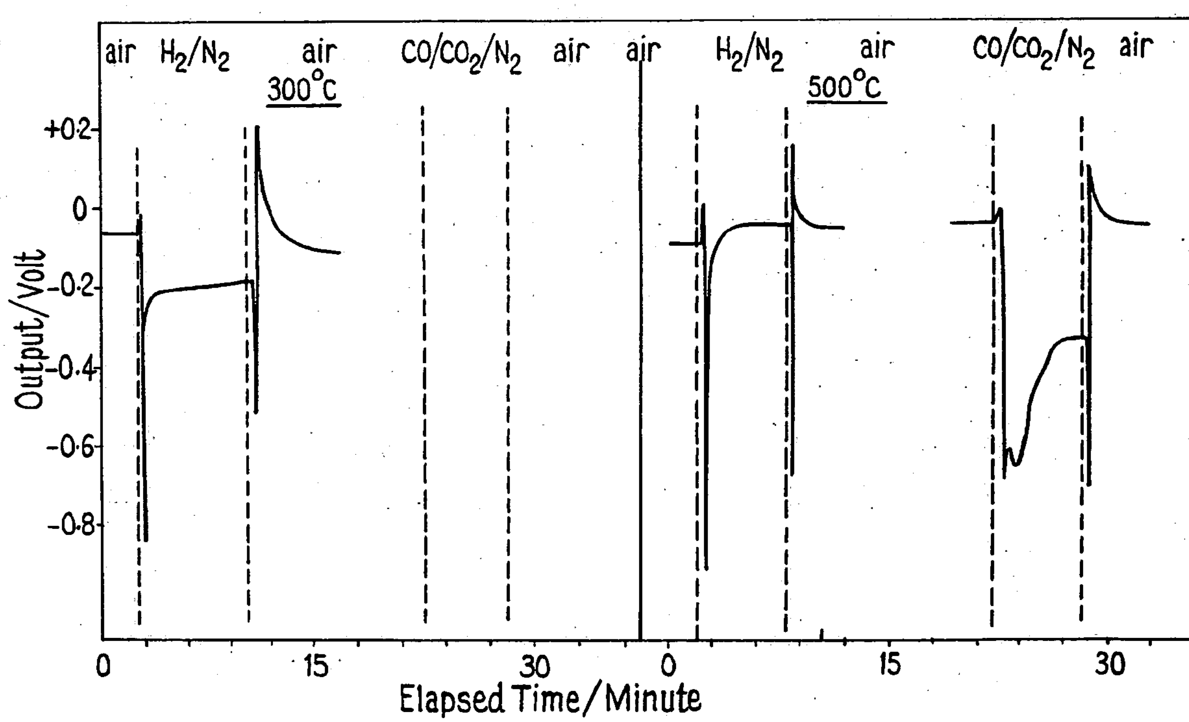
air
H_2/N_2
air
300°C
$CO/CO_2/N_2$
air
air
H_2/N_2
air
500°C
$CO/CO_2/N_2$
air
Output/Volt
+0·2
0
-0·2
-0·4
-0·6
-0·8
0
15
30
0
15
30
Elapsed Time/Minute

FIG.4

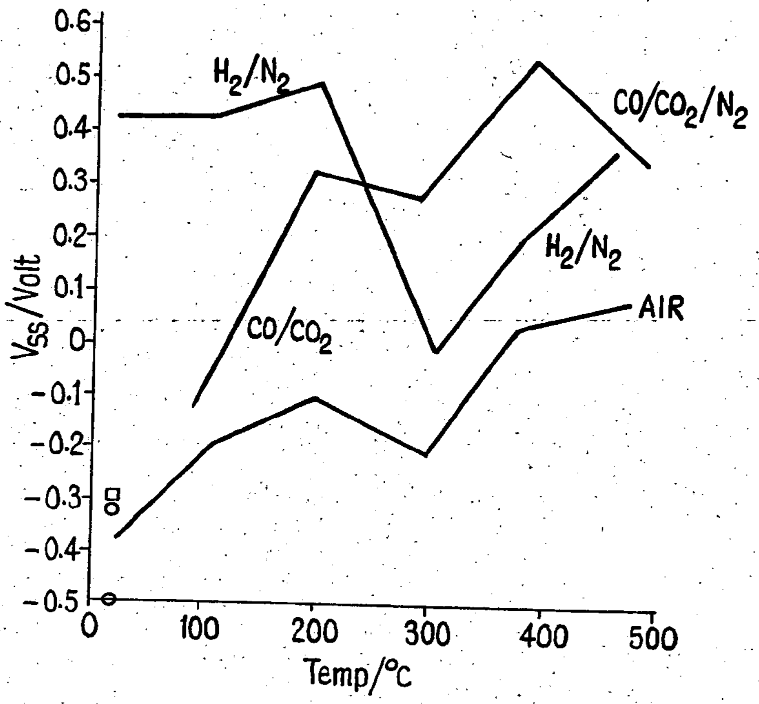

FIG.5

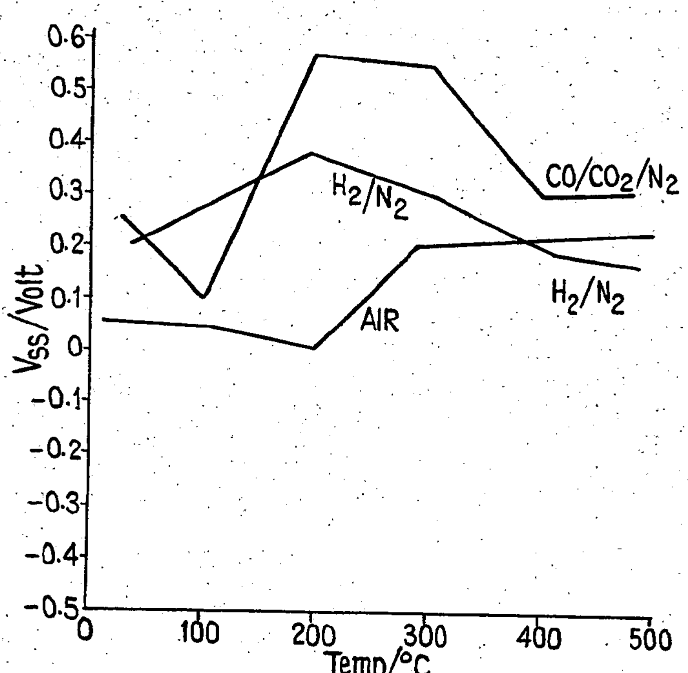

FIG.6

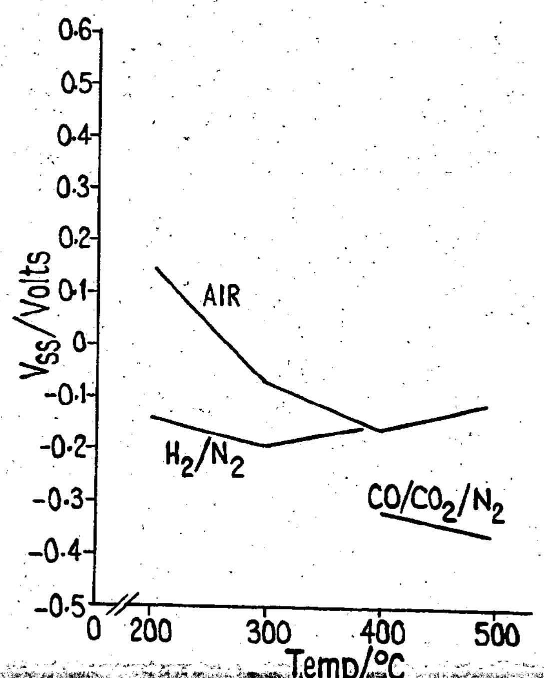

FIG.7

SPECIFICATION

Improvements in r r lating t sensors

The present invention relates to sensors and more particularly to gas sensors suitable for use in gases and gaseous mixtures.

According to one aspect of the present invention there is provided a gas sensor suitable for use in a gas or gaseous mixture comprising a solid electrolyte, in which the mobile ion is other than oxygen, and two or more electrodes in communication with the said solid electrolyte and arranged so as to be capable of being contacted with a common gas or gaseous mixture.

Examples of solid electrolytes in which the mobile ion is other than oxygen are sodium-beta-alumina, hydrogen-beta-alumina and rubidium-beta-alumina.

Preferably the electrodes are arranged to produce a different potential when in contact with the common gas or gaseous mixture such that the sensor is a mixed potential gas sensor. This may be effected, for example, by arranging for the electrodes to be of different size, or by arranging for the electrodes to be of different materials (e.g. Pt or Au or Ni), or by arranging for the rate of diffusion to and/or from one electrode to be different (e.g. by use of a porous diffusion "barrier" at one electrode).

A gas sensor in accordance with the present invention may be used in quantitative and/or qualitative determinations with gases and gaseous mixtures.

The electrodes may be in direct communication with the solid electrolyte by being in contact therewith.

It will be appreciated that the potentials developed at each electrode are due to the electrode reactions with constituents in the gas or gaseous mixture.

Examples of gases and gaseous mixtures which have been used with a gas sensor in accordance with the present invention are air, 30% H_2/70% N_2 (hereinafter abbreviated to "H_2/N_2") and 5% CO/5% CO_2/90% N_2 (hereinafter abbreviated to "$CO/CO_2/N_2$").

When in use in an oxygen containing gaseous mixture the electrode reactions of a gas sensor which give rise to the observable potentials would be expected to involve the exchange of oxygen with the electrolyte. It is surprising therefore that voltage responses are observed in oxygen containing gaseous mixtures such as air with a solid electrolyte in which the mobile ion is other than oxygen.

Also it is surprising that large voltage responses can be obtained at relatively low temperatures (e.g. large responses are shown by sodium-beta-alumina at temperatures of 100°C or less).

According to another aspect of the present invention there is provided a method for effecting determinations in a gas or gaseous mixture which comprises contacting a sensor with the gas or gaseous mixture and measuring the electrical response of the sensor, said sensor comprising a solid electrolyte, in which the mobile ion is other than oxygen, and two or more electrod s in communication with the said solid electrolyte, said electrolyte and said electrodes being in contact with the same gas or gaseous mixture.

The present invention will now be further described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a diagrammatic representation of one form of gas sensor in accordance with the present invention;

Figure 2 is the response, in terms of output voltage and time, of a gas sensor of the form shown in Figure 1 at 300°C and 500°C with the gaseous mixtures indicated using sodium-beta-alumina as the electrolyte and Pt and Au as electrodes;

Figure 3 is the response, in terms of output voltage and time, of a gas sensor of the form shown in Figure 1 at 300°C and 500°C with the gaseous mixtures indicated using H_3O-beta-alumina as th electrolyte and Pt and Au as electrodes;

Figure 4 is the response, in terms of output voltage and time, of a gas sensor of the form shown in Figure 1 at 300°C and 500°C with the gaseous mixtures indicated using Rb-beta-alumina as the electrolyte and Pt and Au as electrodes;

Figures 5, 6 and *7* depict the steady state voltage (Vss) developed by mixed potential gas sensors in accordance with the present invention as a function of temperature for three solid electrolytes (using Pt and Au electrodes) with a selection of gaseous mixtures. In the case of Figure 5 the solid electrolyte was sodium-beta-alumina, in the case of Figure 6 the solid electrolyte was hydrogen-beta-alumina and in the case of Figure 7 the solid electrolyte was rubidium-beta-alumina.

Referring now to Figure 1 of the drawings there is shown a gas sensor comprising a solid electrolyte 1 in which the mobile ion is other than oxygen, and, in contact with the solid electrolyte 1 a platinium electrode 2 and a gold electrode 3. (The solid electrolyte may be carried by a substrate (e.g. of alumina) (not shown)).

Conductors 4 and 5 are provided to connect the electrodes to a voltage measuring means 6 (e.g. a millivoltmeter) for measuring the output voltage from the gas sensor.

In operation a gas or gaseous mixture is contact d with the solid electrolyte 1 and with the electrodes 2 and 3.

The output voltage is measured by the voltage measuring means 6. Changes in the composition of the gas or gaseous mixture which result in a change of output voltage are observed as changes in the voltage recorded by the voltage measuring means 6.

Referring now to Figures 2 to 4 the solid electrolyte used in each case was approximately 20mm × 5mm × 2mm (thickness). To prepare the sensors wire of th electrode metal was wound around ach end of the solid electrolyte and electrodes painted over the wire and onto the surface of the electrolyte in a strip approximately 5 mm wide.

The responses were obtained by placing the gas sensors in a tube furnace in a gas stream of ~ 100ml/1 minute. The voltage developed was measured with an electrometer and display d on a chart recorder.

Two main aspects of response wer observed

when the gaseous mixture was changed. Firstly a spike was observed (the voltage traversing rapidly first in one direction, then in the other with amplitude sometimes up to ± 1 V) during the time that both gaseous mixtures were present together in the vicinity of the sensor. Secondly, there was a change in the steady state voltage delivered by the sensor. Steady state voltages plotted against temperature for various materials with Pt and Au electrodes are shown in Figures 5 to 7 inclusively. The responses of devices having different electrolyte materials to the various gas changes were different. Thus, for electrodes of Pt and Au, a sensor having a Rb-beta-alumina electrolyte above 300°C showed little voltage change when the test gas was changed between air and H_2/N_2 but produced a large voltage change for a gas change between air and $CO/CO_2/N_2$.

In contrast sensors with a sodium-beta-alumina electrolyte showed large temperature sensitive steady state output voltages for air, H_2/N_2 and $CO/CO_2/N_2$ at temperatures of 200°C and over. At lower temperatures, the response to a change between air and $CO/CO_2/N_2$ became extremely sluggish and the steady state output voltage change became small; in these circumstances there was a large and rapid voltage output change in response to a change from $CO/CO_2/N_2$ to H_2/N_2. Sensor devices with a sodium-beta-alumina electrolyte gave a large response at temperatures of 100°C or less when the gas was changed between air and H_2/N_2. Sensors with hydrogen-beta-alumina electrolyte behaved diff rently. Thus, such sensors showed virtually no steady state voltage change with temperature for any of the gases at temperature 400°C and over, but at lower temperatures the response was similar to that of sensors with a sodium-beta-alumina electrolyte.

The steady state voltage developed in $CO/CO_2/N_2$ atmosphere was unaffected by the presence of water vapour. The voltage developed in H_2/N_2 or in air is influenced by the presence of water vapour in a fashion dependent on the temperature and the electrolyte.

CLAIMS

1. A gas sensor suitable for use in a gas or gaseous mixture comprising a solid electrolyte, in which the mobile ion is other than oxygen, and two or more electrodes in communication with the said solid electrolyte and arranged so as to be capable of being contacted with a common gas or gaseous mixture.

2. A gas sensor as claimed in claim 1 wherein the solid electrolyte is sodium-beta-alumina, hydrogen-beta-alumina or ribidium-beta-alumina.

3. A gas sensor as claimed in claim 1 or claim 2 wherein electrodes are arranged to produce a differ nt potential when in contact with the common gas or gaseous mixture such that the sensor is a mixed potential gas sensor.

4. A gas sensor as claimed in claim 3 wherein electrodes are arranged to be of different size.

5. A gas sensor as claimed in claim 3 wherein electrodes are arranged to be f different materials.

6. A gas sensor as claimed in claim 3 wherein the rate of diffusion to and/or from one electrode is arranged to be different from another electrode.

7. A gas sensor as claimed in any one of the preceding claims wherein the electrodes are in direct communication with the solid electrolyte by being in contact therewith.

8. A gas sensor as claimed in any one of the preceding claims wherein an electrode is platinum or gold or nickel.

9. A gas sensor as claimed in any one of the preceding claims comprising a solid electrolyte in which the mobile ion is other than oxygen, and, in contact with the solid electrolyte, a platinum electrode and a gold electrode said platinum electrode and said gold electrode each having a conductor for connecting the said electrodes to a voltage measuring means.

10. A method for effecting determinations in a gas or gaseous mixture which comprises contacting a sensor with the gas or gaseous mixture and measuring the electrical response of the sensor, said sensor comprising a solid electrolyte, in which the mobile ion is other than oxygen, and two or more electrodes in communication with the said solid electrolyte, said electrolyte and said electrodes being in contact with the same gas or gaseous mixture.

11. A gas sensor substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

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